

Effect of Substrate Roughness on Contact Angle of Sputter Deposited Superhydrophobic PTFE Coatings

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Abstract

Polytetrafluoroethylene (PTFE) superhydrophobic coatings were prepared using magnetron sputtering process. The PTFE coatings were deposited on sand blasted glass substrates with different substrate roughnesses (R_a) in the range of 50 - 7000 nm. The PTFE coatings were characterized using X-ray diffraction, X-ray photoelectron spectroscopy, field emission scanning electron microscopy, contact angle analyzer and atomic force

microscopy techniques. The PTFE coatings deposited on sand blasted glass substrates ($R_a = 4500-4800$ nm) were found to be superhydrophobic with a static contact angle of 152° and a low contact angle hysteresis (2°). The superhydrophobicity observed in these coatings is attributed to the presence of dual scale roughness, densely packed microstructure and the presence of CF_3 groups.

1.0. Introduction

Wettability of solid surfaces is an important property and depends on both the surface free energy and the surface roughness. A material with low surface free energy (e.g., regularly aligned closest hexagonal packed – CF_3 groups) deposited on a flat surface exhibits a maximum contact angle of 119° ¹. By introducing a suitable roughness on a flat surface, a water contact angle of more than 150° has been achieved ²⁻⁴. The effect of roughness on the wettability of solid surfaces has been described by the well known Wenzel and Cassie-Baxter models ^{5,6}. According to Wenzel, the liquid droplet retains contact at all points with the solid surface below it, whereas, in the Cassie-Baxter state, the drop rests on the peaks of surface protrusions and bridges the air gaps in between ^{5,6}.

It has been widely reported that a dual-scaled roughness (i.e., micron and nanometer scale) enhances superhydrophobicity significantly ^{7,9}. The lotus leaf is a well-known example of a naturally occurring superhydrophobic surface exhibiting dual scale roughness ¹⁰. A combination of micro- and nano-scaled structure builds two-level roughness which modifies a certain coefficient in Wenzel and Cassie-Baxter equation, thus resulting in a contact angle value which is much larger than those having a single level of roughness ¹¹. Recently, numerous studies have confirmed that dual scale roughness combined with a low surface free energy material leads to a water contact angle greater than 150° and a low sliding angle ⁷⁻⁹. Among the materials exhibiting low surface free energy, polytetrafluoroethylene (PTFE) has the lowest surface free energy (18.5 mN/m) and is therefore best suited for superhydrophobic applications.

In this paper, we have evaluated the wettability of PTFE coatings deposited on untreated, plasma etched and sand blasted glass substrates. The PTFE coatings (nanoscale roughness) on untreated, plasma

etched and sand blasted glass substrates (micro level roughness) were deposited using radio frequency (RF) magnetron sputtering. The effect of substrate roughness and argon flow rate on the apparent contact angle has been studied. Field emission scanning electron microscopy (FESEM), x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), contact angle analyzer and atomic force microscopy (AFM) techniques have been used to characterize the superhydrophobic PTFE coatings.

2.0. Experimental Details

The PTFE coatings were deposited on borosilicate glass substrates (untreated, plasma etched and sand blasted) using RF magnetron sputtering. The borosilicate glass slides were sand blasted using $40 \mu\text{m}$ grit size alumina. Three sets of PTFE coatings were prepared. In the first set, the PTFE coatings were deposited on untreated glass substrates and the Ar flow rate was varied from 17-30 sccm. In the second set, the PTFE coatings were deposited on glass substrates which were plasma etched at different durations. In the third set, the PTFE coatings were deposited on various sand blasted glass (SBG) substrates with average roughness (R_a) values ranging from 500-7000 nm. Before placing the substrates in the vacuum chamber, the substrates were chemically cleaned in an ultrasonic agitator in absolute alcohol and trichloroethylene. The vacuum chamber was pumped down to a base pressure of $5.0 \times 10^{-4} \text{ Pa}$. The PTFE coating was deposited by sputtering a PTFE target in Ar plasma using RFX-600 and ATX-600 RF generators (frequency = 13.56 MHz). The partial pressure of Ar gas (approximately 1.0 Pa) was controlled in order to achieve nanometer scale surface roughness. The thickness of the PTFE coating was approximately $1 \mu\text{m}$.

The roughness of the sand blasted glass substrates was measured using Mitutoyo surface roughness tester (SURFTEST 301).

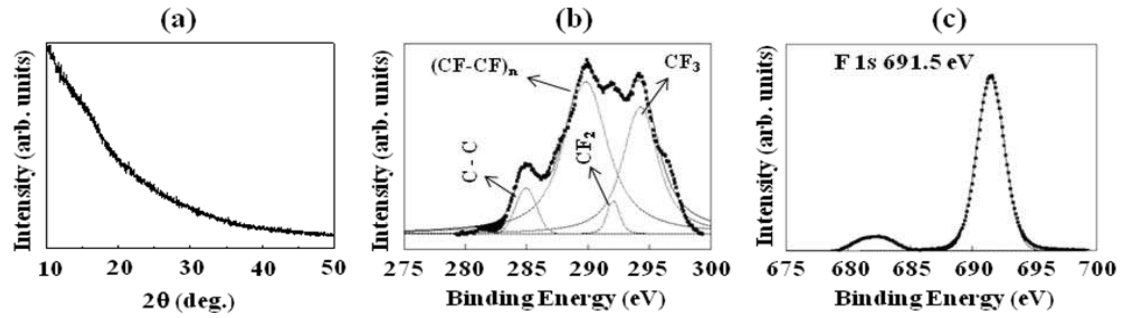


Fig. 1: (a) XRD pattern for sputter deposited PTFE coating, core level XPS spectra of (b) C 1s peak and (c) F 1s peak of as-deposited PTFE coating

XRD patterns of the coating were recorded in a Rigaku D/max 2200 Ultima X-ray powder diffractometer with thin film attachment. The X-ray source was a Cu K α radiation ($\lambda = 0.15418$ nm), which was operated at 40 kV and 30 mA. The bonding structure of the coatings was characterized by XPS using an ESCA 3000 (V.G. Microtech) system with a monochromatic Al K α X-ray beam (energy = 1486.5 eV and power = 150 watts). The surface morphology of the coating was observed using atomic force microscopy (Surface Imaging Systems) and field-emission scanning electron microscopy (Carl-Zeiss) techniques. The static contact angle (CA) was measured according to the sessile drop method using a contact angle analyzer (Phoenix 300 goniometer) with deionized water. The droplet size of the fluids was about 5 μ L, so that the gravitational effects are neglected. The contact angle of the samples was measured at several places and the values reported herein are the averages of three measurements.

3.0. Results and Discussion

3.1. Structural Characterization

Fig. 1(a) shows the XRD data of 1 μ m thick PTFE thin film deposited on silicon substrates (glancing angle = 1°). The absence of crystalline peaks corresponding to PTFE

indicates that the coating is X-ray amorphous. However, the XPS data clearly showed that the chemical composition of the deposited coating was similar to that of PTFE. The core level spectra of C 1s and F 1s are shown in Figs. 1(b) and 1(c), respectively. Deconvolution of the C 1s spectrum showed the presence of four peaks corresponding to C-C (285 eV), CF-CF_n (289.3 eV), CF₂ (292 eV) and CF₃ (295 eV). Similarly, the F 1s spectrum showed a high intensity peak centered at a binding energy of 691.5 eV, which corresponds to F in CF-CF_n. In the XPS data, we observed very distinct CF₃ and CF-CF_n peaks. It is known that, a surface terminated with -CF₃ radical has a lower surface free energy than a surface terminated with -CF₂ radical². The excess CF₃, CF-CF_n groups and the fluorine rich surface lower the surface free energy of the PTFE coatings, resulting in an increase in the contact angle.

3.2. PTFE coatings deposited on untreated glass substrates

The PTFE coatings were deposited on untreated glass substrates ($R_a = 50$ nm) for different Ar flow rates ranging from 17-30 sccm. Table 1 shows the effect of Ar flow rate on the contact angle of PTFE coatings. Fig. 2(a-c) shows the three dimensional AFM images of the PTFE coatings deposited at Ar flow rates of 17, 25 and 30 sccm, respectively.

Table 1. Effect of Ar flow rate on the contact angle of PTFE coatings deposited on untreated glass substrates

Ar flow rate (sccm)	Operating pressure (mbar)	Power (W)	Duration (min)	R _a (nm)	Static Contact Angle (°)
17	1×10 ⁻²	75	45	4.0	95
25	1×10 ⁻²	75	45	29.0	120
30	1×10 ⁻²	75	45	7.9	113

A maximum contact angle of 120° was achieved for coatings deposited at an Ar flow rate of 25 sccm with a target power of 75 W.

This is due to the nano-needle like morphology of the PTFE coating which is shown in Fig. 2b. The rms roughness of the corresponding coating is 29 nm. Further increase in the Ar flow rate resulted in decrease in both the roughness (7.9 nm) and the contact angle values (113°). These results clearly showed that the contact angle values are strongly affected by the surface topography and surface roughness.

3.3. PTFE coatings deposited on plasma etched glass substrates

In order to enhance the hydrophobicity, a suitable substrate roughness is required and the untreated glass substrates were roughened using plasma etching technique. The glass substrates were etched in Ar plasma, and the Ar flow rate, substrate bias and duration were varied in order to obtain different substrate roughnesses.

The optimized process parameters for etching were: substrate bias: -1000 V, Ar flow rate - 30 sccm, substrate temperature - 150°C and the duration -2 hrs.

Figs. 3(a-c) show the three dimensional AFM images of untreated glass, Ar plasma etched (PE) glass substrate and PTFE coating deposited on PE glass substrate, respectively. The AFM images (Figs. 3b and 3c) clearly show the nano- needle like morphology grown

perpendicular to the surface. The PE glass substrate showed a root mean square roughness value of 8.5 nm with a contact angle of 55°. Whereas, the PTFE coating deposited on the PE substrate (R_a = 20 nm) exhibited a contact angle of 110°, which is less than the coating deposited on untreated glass substrate (120°). The decrease in the contact angle maybe due to the incorporation of polar contaminants and roughening of the surface as Wenzel's equation predicts the increase in hydrophilicity with roughness when the smooth surface have contact angle below 90°⁴. These results clearly showed that the nano-level surface roughness (single level roughness) alone is not sufficient to achieve the superhydrophobicity.

3.4. PTFE coatings deposited on sand blasted glass substrates

3.4.1. Effect of substrate roughness

In order to achieve superhydrophobicity, the PTFE coatings were deposited on sandblasted glass substrates at different substrate roughness ranging from 500–7000 nm.

Fig. 4 clearly shows the effect of substrate roughness on the contact angle. It is clear from Fig. 4 that increasing the substrate roughness in the range of 4500–4800 nm gives the highest water contact angle.

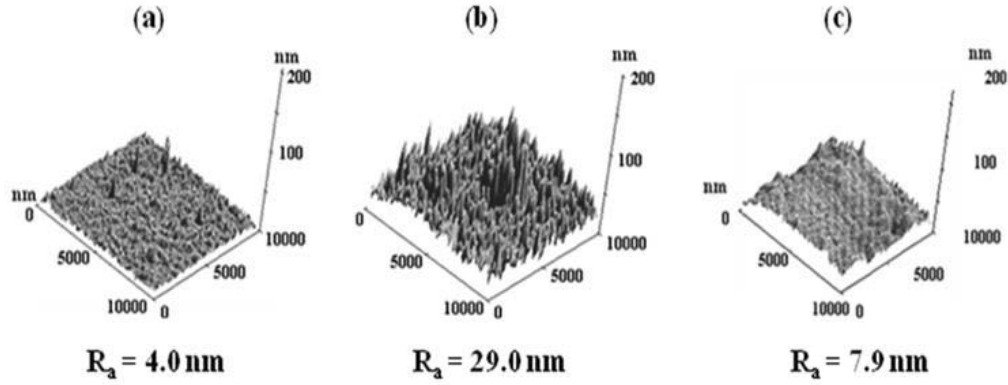


Fig. 2: Three dimensional AFM images of PTFE coatings deposited at (a) 17 sccm (b) 25 sccm and (c) 30 sccm.

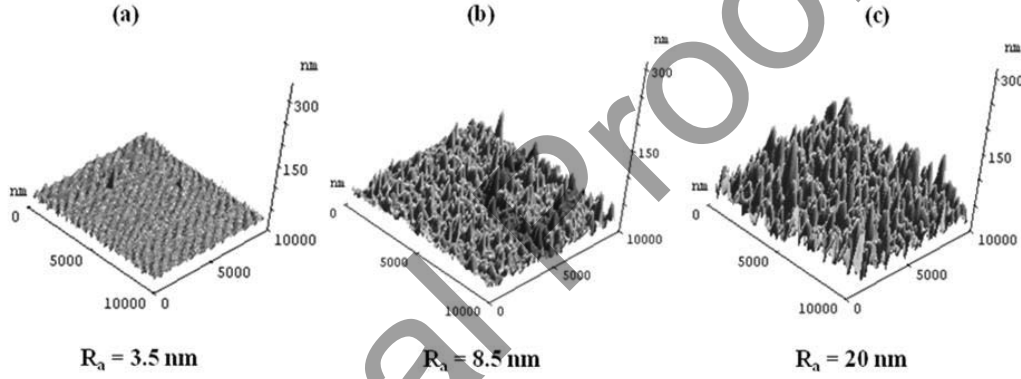


Fig. 3: Three dimensional AFM images of (a) untreated glass (b) Ar plasma etched glass substrate and (c) PTFE coatings deposited on the PE glass substrate

For samples with $R_a = 4500-4800$ nm, water contact angle as high as 152° was achieved, with very low contact angle hysteresis of 2° . This clearly shows that the droplet was in Cassie-Baxter state and this is due to the micron scale substrate roughness combined with nano-scale roughness of the PTFE coating. It is also believed that for these samples the asperities were spaced closed enough so that the droplet was stable in Cassie-Baxter state. This was supported by surface roughness profile data as shown in Fig. 5(a) (explained below). Further increasing the substrate roughness, $R_a > 4800$ nm, resulted in a decrease in the contact angle value (e.g., 125° for $R_a = 7000$ nm). It is because at higher substrate roughness values (5300-7000 nm) the

liquid drop collapses between the asperities and follows the surface topography existing in the Wenzel state. It could be inferred that by sand blasting of glass substrate to generate a substrate roughness in the range of 4500–4800 nm there is a 26% increase in the apparent contact angle of PTFE coatings. Furthermore, this value of substrate roughness is the optimized value for superhydrophobicity in the Cassie-Baxter regime due to the high water contact angle and low hysteresis. The high CA depends on a high percentage of liquid-solid interfaces replaced by liquid-gas interfaces⁹. It has been reported that the dual scale rough surface traps more air fractions than surfaces having one level of roughness (micro (or) nano level roughness)⁹.

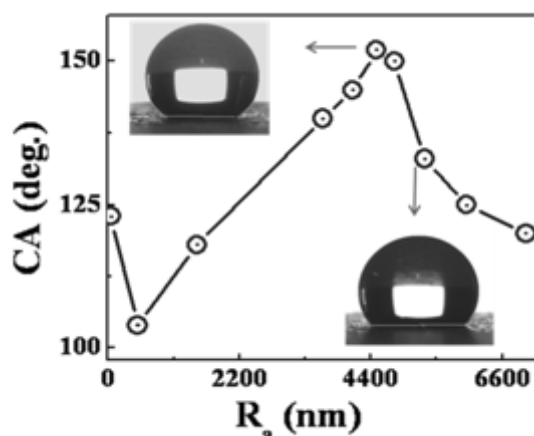


Fig. 4: Effect of substrate roughness on the contact angle of PTFE coatings deposited on sand blasted glass substrates.

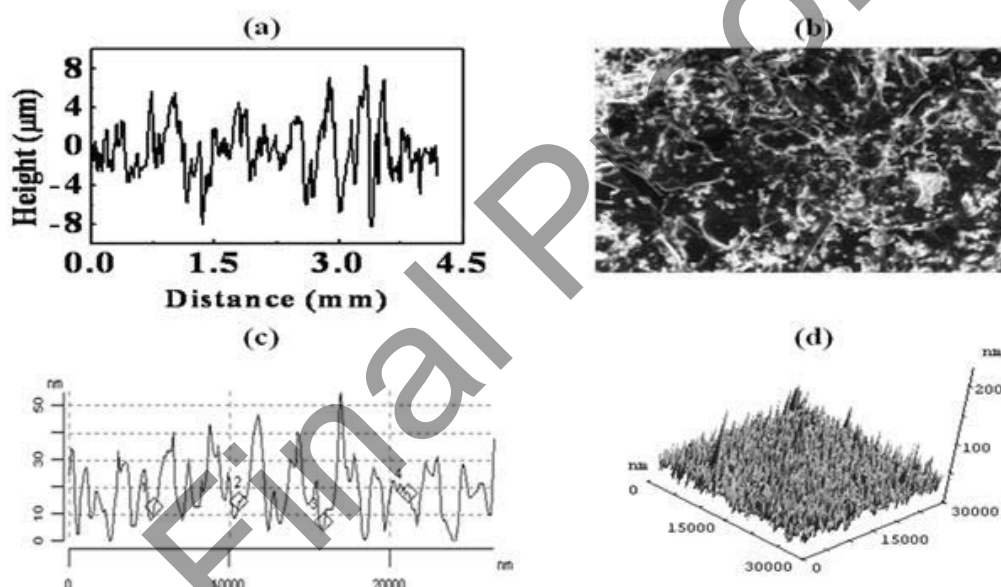


Fig. 5: (a) Typical surface profile of a glass substrate after sand blasting (b) FESEM image of PTFE coating deposited on sand blasted glass substrate (c) Typical AFM surface profile of PTFE coating showing nano-level roughness ($R_a = 20$ nm) and (d) Three dimensional AFM image of PTFE coating.

The presence of dual scale roughness is evident from Fig. 5. Fig. 5(a) shows the roughness profile of a glass substrate with $R_a = 4500$ nm. The roughness profile displayed regular peaks and troughs and the average distance between adjacent peaks was approximately 200-300 μm . The low magnification FESEM image of the PTFE thin film deposited on the glass substrate ($R_a = 4500$ nm) is shown in Fig. 5(b), exhibiting

fractal-like microstructure. The roughness profile of PTFE coating deposited on an untreated glass substrate (Fig. 5(c)) clearly shows the presence of nano-level roughness with an RMS roughness of 20 nm. The corresponding three dimensional AFM image is presented in Fig. 5(d). These results confirmed that the presence of dual scale roughness combined with high concentration of CF_3 groups along with CF-CF_n groups

(explained earlier) lower the surface free energy of the PTFE coatings rendering them superhydrophobic.

4.0. Conclusions

- The PTFE coatings deposited on untreated and plasma etched glass substrates (nano-level roughness) showed a maximum contact angle of 120°. This clearly shows that single level surface roughness is not sufficient to achieve superhydrophobicity.
- The PTFE coatings deposited on sandblasted glass substrate ($R_a = 4500$ nm) exhibited a high contact angle of 152° and a low contact angle hysteresis of 2°.
- The superhydrophobicity was achieved by the dual scale roughness which can trap more air fractions than the single level roughness.
- The presence of dual scale roughness was clearly confirmed by the FESEM and the AFM images.
- The presence of CF-CF_n, CF₂ and CF₃ groups in the PTFE coating was confirmed by the XPS data. The CF₃, CF-CF_n groups and the fluorine rich surface lower the surface free energy of the PTFE coatings resulted in increase in the contact angle.

5.0. References

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